

Trends in the Gravimetric and Volumetric Energy Densities of Lithium-Ion Batteries over the Past Decade

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Abstract: *The demand for lithium-ion batteries, owing to their diverse applications such as in electric vehicles, aerospace, and electronic devices, has increased rapidly through the years. Since the first prototype of the Lithium-ion battery in 1985, new versions of the Li-ion battery have seen changes and modifications to the structure of the battery, particularly in the cathode and anode used. These, in turn, have increased efficiency and commercial viability in various ways, including by allowing for higher energy densities. This paper analyses trends in the volumetric and gravimetric energy densities of lithium-ion batteries from 2012 to 2022, ascertained using research papers which discuss lithium-ion batteries, and the implications of the evolution of these metrics.*

Keywords: Lithium-ion Batteries, Volumetric Energy Density, Gravimetric Energy Density, Energy Density, Specific Energy

1. Introduction

A standard Li-ion battery consists of a cathode (the negative electrode), an anode (the positive electrode), and an electrolyte. In the charging process, the lithium ions move from the positive to the negative electrode, while in the discharging process they detach from the negative electrode and penetrate the positive electrode, moving through the electrolyte. Historically, carbon-based anodes have been used in lithium-ion batteries, but in modern times, other materials such as silicon and alloy materials like tin have emerged as alternatives.

Various studies in recent years have reflected on the issues currently associated with Li-ion batteries, such as the efficiency of their functioning in conditions of extreme temperatures, the safety risks associated with them, and the access to charging devices. Furthermore, several papers have explored and analysed the future prospects in this field, making hypotheses related to the efficiency of the next generation of Li-ion batteries. Nonetheless, over the years, various attributes of these rechargeable batteries have been changed and improved upon, including both gravimetric and volumetric energy density, charge/discharge rates, and cycle life.

Volumetric energy density refers to energy stored per unit volume. It serves to allow one to gauge the storage space required for the fuel, which is a factor one must consider in order to utilise the fuel in real-life applications. In the context of electric vehicles, for instance, more volumetric energy density translates to allow the vehicle to traverse a larger range with a battery pack of the same size.

Gravimetric energy density refers to energy stored per unit mass. It is a measure of energy efficiency which is used both in fuels and in defining capacities in batteries. A high gravimetric energy density, or specific energy, can prove to be useful in electric applications of the lithium-ion battery e.g., it

allows for lightweight mobile phones.

While both metrics are important indicators of the quality of a fuel or battery, volumetric energy density is used more commonly, since there are fewer applications of lithium-ion batteries, or batteries in general, which are weight-sensitive. Volumetric energy density is therefore used synonymously with energy density, and more carefully considered to analyse the performance of a battery. In order to avoid confusion, this paper will utilise 'volumetric energy density' in lieu of just 'energy density', and 'gravimetric energy density' in lieu of 'specific energy'.

A simplified way to calculate gravimetric energy density, which is often used for estimation purposes, involves multiplying the theoretical cell voltage with the specific charge. Similarly, volumetric energy density is calculated by multiplying the theoretical cell voltage with the charge density.

Both these measures have theoretical values, which can be calculated using the means above, and practical values, which are the values obtained in practice. It is common for the practical gravimetric and volumetric energy densities to be 25 to 30% lower than their theoretical counterparts. This difference arises because of the discrepancy between the actual cell voltage and the theoretical cell voltage.

As previously stated, the anode material used in a lithium-ion battery significantly influences its properties, including the gravimetric and volumetric energy density. This occurs because the redox or reduction potential of the anode material, which measures the ease with which electrons will be accepted by the anode material, will influence its cell voltage, which as seen above, determines both gravimetric and volumetric energy densities. [1]

Since the anode materials have been changed throughout the history of lithium-ion batteries and technology has improved,

the gravimetric and volumetric energy densities have also changed. Several research articles have detailed the qualitative changes in lithium-ion batteries since the first instance of commercialization in 1991 by Sony, but none feature a clear focus on the change in energy densities by utilising the real values over the years. [2][3][4] This paper presents an analysis of the trends in the densities in the past decade.

2. Methodology

In order to investigate how gravimetric and volumetric energy densities of lithium-ion batteries have changed over the years, as well as to understand the consequences of these changes, values for the two measures were obtained using academic research papers. To gain access to relevant research papers more promptly, specifically those which supported analyses with numerical values of the energy densities, Google Scholar and the artificial intelligence tool Elicit were intermittently utilised. Once these values were collected, the values over the years were plotted, allowing for multiple values within a year, and then analysed with respect to the technological changes that were required to reach those levels of gravimetric or volumetric energy densities.

Theme

Volumetric Energy Density

The volumetric energy density of any battery is an essential determinant of its viability as an energy source. The volumetric energy density, in general, of lithium-ion batteries is one of the reasons for its popularity in diverse fields.

Gravimetric Energy Density

The gravimetric energy density of a battery is essential when a device must be used for extended periods of time, but in most applications, is given less priority as compared to volumetric energy density. The theoretical gravimetric energy densities of lithium-ion batteries are much higher than their practical counterparts, owing to the safety risks currently associated with gravimetric energy densities of a certain level.

3. Findings and Discussion

In 2012, the gravimetric energy density attained in laboratory settings was 150 Wh/kg [5]. This indicated significant progress from the performance of lithium-ion batteries in the 20th century, in their nascent stage, where gravimetric energy density was at about 80 Wh/kg. This was made possible through various enhancements, including making the anode more graphitic and reducing the surface area. [2] Tangentially, the progress made was primarily in aqueous lithium batteries, which have lower energy densities and cycle lives than solid-state lithium-ion batteries, but were more commercially popular at the time.[6]

In 2013, as seen in the data, gravimetric energy density noted was 185 Wh/kg[7]. While this was an increase from the previous year, experts noted that lithium-ion batteries

remained too heavy to be used practically in electric vehicles. Moreover, it was noted that the graphite-based anodes that were being used, while beneficial for being able to allow for high cell potential, were leading to a significant amount of safety concerns in using the batteries.[8]

2014 marked an important milestone in the rise of Lithium-ion batteries, as the corporations Tesla and Panasonic created plans for an LIB manufacturing plant. The energy densities, at this point in time, hovered at around 600 Wh/L [9] and 200 Wh/kg[10]. This increase was possible as a result of the first-ever large-scale incorporation of a silicon anode. The battery in question, from Amprius Corp, was also a commercial success.

In 2015, the gravimetric and volumetric energy densities recorded were 500 Wh/L [11] and 200 Wh/kg [11]. Various breakthroughs occurred in using intercalation materials such as lithium cobalt oxide and lithium nickel cobalt aluminium oxide. Notably, the use of lithium titanium oxide as an anode allowed for a volume change of only 0.20 %, high volumetric capacity, as well as higher thermal stability.[12] However, the more important change that occurred in lithium-ion batteries was in the cathode, which was made more efficient through structural changes, such as by using nanomaterials. [13]

In 2016, the gravimetric energy density was boosted to 258 Wh/kg [14] while volumetric energy density was augmented to reach 650 Wh/L[15]. Correspondingly, the corporation BYD recorded the highest yet sales volume of electric vehicles. In terms of the battery itself, nickel-rich cathodes, which had higher capacities, were commercially implemented, but issues related to thermal stability and cycle stability prevailed.[16]

In 2017, there was no significant change in either gravimetric or volumetric energy density[17]. However, research and improvements in silicon as an anode for lithium-ion batteries continued to be made. Its electrochemical performance was improved significantly using nanostructures, but there were various issues preventing further progress, including the higher cost of production due to the incorporation of nanomaterials.[18]

In 2018, the volumetric energy density increased to 700 Wh/L[19], which may have compromised the gravimetric energy density, which was recorded at 220 Wh/kg[20]. Nickel and manganese-rich cathodes were being both used and researched extensively, allowing for higher thermal stability as the gravimetric and volumetric energy densities increased. [21]

In 2019, there was no significant change in either volumetric or gravimetric energy density. Solid-state lithium-ion batteries became more popular, since they helped mitigate issues associated with safety in aqueous lithium-ion batteries. [22]

In 2020, data from research indicated that the volumetric energy density was 620 Wh/L [23], while gravimetric energy

density increased to 400 Wh/L [24]. In parallel, electric vehicles sales reached 2 million globally. Furthermore, structural changes, including a ceramic separator between the anode and the cathode in a solid-state battery, were made to reduce charging time, increasing commercial viability [25].

In 2021, the volumetric energy density increased to 730 Wh/L while the gravimetric energy density attained was 300 Wh/kg.[26] Commercially, the popularity of lithium-ion batteries grew significantly, and it was predicted that their capacity would increase to five times that of their capacity in 2021. Moreover, lithium-iron-phosphate batteries started to grow commercially. This can be attributed to higher thermal stability due to bond strength, which in turn allows for safer usage of the battery. [27]

In 2022, NanoGraf Technologies’ battery, the Li-ion 18650

battery, reached a milestone for both volumetric and gravimetric energy density, at 1150 Wh/L and 450 Wh/kg respectively [28]. Notably, the most recent version of the Lithium-Ion battery used silicon anodes, allowing for the sharp rise in energy densities. The lightness of silicon, in comparison with the graphite or alloys of nickel and cadmium that were previously utilised, allows for a rise in gravimetric energy density while its ability to store large amounts of energy (nearly 10 times that of graphite) permits a rise in volumetric energy density. However, silicon’s ability to expand greatly in volume makes it prone to breaking apart, compromising the number of life cycles of the battery. Furthermore, electrical conductivity is at risk when silicon anodes are used, as silicon may form alloys with lithium, leading to cracking and therefore, reduced electrical conductivity [29].

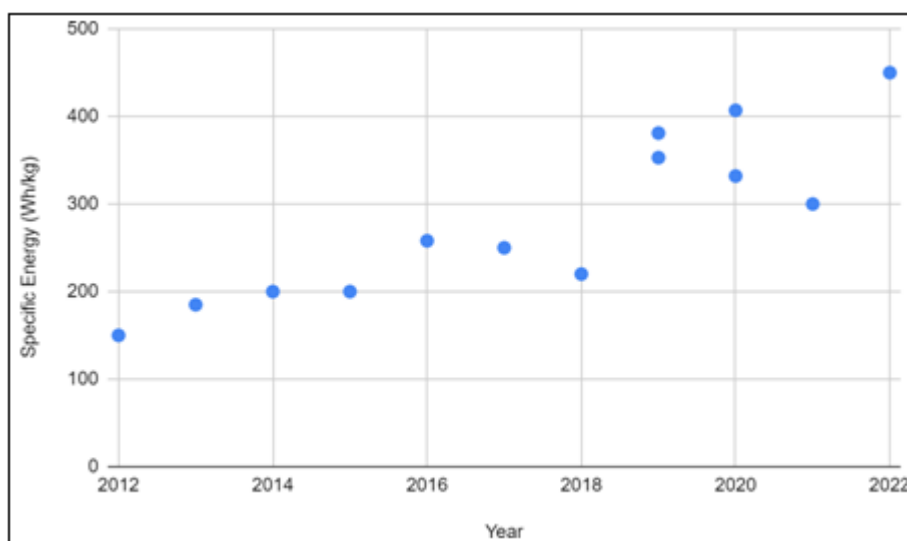


Figure 1: Trend in Gravimetric Energy Density

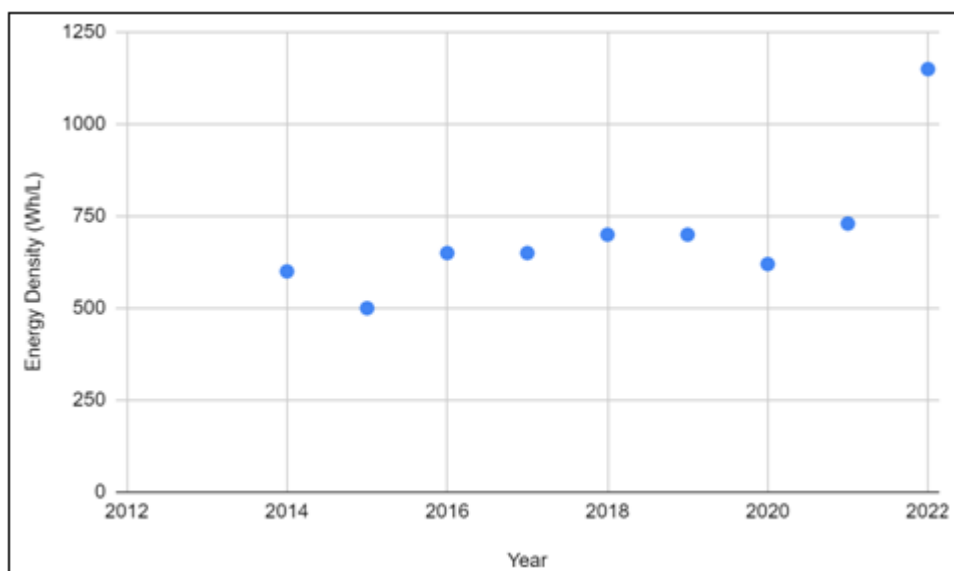


Figure 2: Trend in Volumetric Energy Density

Overall, the trend observed was, predictably, a steady increase in both the gravimetric and volumetric energy densities, owing to various technological developments, as seen in the graphs above. Fig 1 and Fig 2 represent the gravimetric and volumetric energy densities, respectively, from the year 2012 to 2022.

This increase was aided by the portable electronics revolution (which was only possible due to LIBs) and the increase in sales of electric vehicles. As the production scale and demand as a result of consumer awareness about sustainability grow, electric vehicle sales are expected to grow to secure 32% of the total market share for new car sales.[30] Moreover, throughout the energy density data, it was apparent that, on average, anode materials made of silicon or phosphorus proved to be more appropriate for attaining higher volumetric and gravimetric energy densities compared to the traditional graphite electrodes.

4. Conclusion

In summary, owing to technological advances as well as developments in cathodic and anodic chemistry of lithium-ion batteries, the gravimetric and volumetric energy densities have increased drastically, with current energy densities surpassing theoretical energy densities from even 2021. The future prospects for further increase in energy density remain promising. In 2023 itself, it was reported that researchers from the Chinese Academy of Sciences were able to reach a volumetric energy density of 1653.65 Wh/L and a gravimetric energy density of 711.30 Wh/kg[31]. This was achieved using a lithium-rich manganese-based cathode, which allows for a significantly high gravimetric energy density. While this was in a laboratory setting and is yet to be used commercially, it incorporated various modifications and technologies to the anode, cathode, electrode leading mass, and other components like separators and collectors, which can be adopted in future batteries.

However, the underlying issue with the ever-improving energy densities of lithium-ion batteries lies in safety. A majority of the applications of lithium-ion batteries require fast-charging, be it electronic appliances or electric vehicles. Using fast-charging infrastructure with high energy-density batteries poses a higher risk to their safe usage. Since the demand for even higher energy densities in lithium-ion batteries will only increase, it is essential to implement structural changes to permit higher energy density batteries to be safe for usage. As a result, solid-state lithium batteries are promising alternatives to traditional lithium-ion batteries, since they remove the safety risk of liquid electrolytes by increasing thermal stability. Alternatively, mechanisms such as incorporating materials with higher thermal conductivity in order to allow for rapid heat diffusion could also reduce heating caused as a result of overcharging.

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